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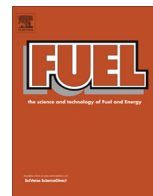
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# Down-hole heavy crude oil upgrading by CAPRI: Effect of hydrogen and methane gases upon upgrading and coke formation <sup>☆</sup>



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## HIGHLIGHTS

- Catalytic heavy oil upgrading was studied experimentally with different gas feeds.
- The effects of hydrogen, methane, gas mixture and nitrogen were examined.
- Upgrading in terms of API gravity was in the order  $H_2 > CH_4 > \text{gas mixture} > \text{nitrogen}$ .
- Differences in viscosity and boiling point range were also detected.
- Lower coke deposit upon the catalyst occurred under hydrogen and methane.

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## ABSTRACT

Heavy oil and bitumen resources will need to be exploited to supplement depleting conventional oils worldwide as they gradually approach their peak production in the forthcoming decades. However, the physico-chemical characteristics of heavy oil and bitumen include high density, low distillates fraction, high viscosity, and high hetero-atom content which make extraction difficult and relatively expensive. The Toe-to-Heel Air Injection (THAI) and 'add-on' Catalytic upgrading process in situ (CAPRI) were specifically developed for the recovery and upgrading of heavy oil and bitumen. In this study, the effects of reaction gas media used in THAI–CAPRI were investigated, in particular the effects of using hydrogen, methane, nitrogen, and a blended gas mixture to simulate THAI combustion gases with Co–Mo/ $\gamma$ - $Al_2O_3$  catalyst at a reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil ratio 50 mL mL<sup>−1</sup>. Ex situ regeneration of the spent catalyst by thermal oxidation of the asphaltenes and coke deposits was also investigated. It was found that the average changes in API gravity of the produced oil were 4° using hydrogen, 3° with methane, 2.9° with THAI gas, and 2.7° with nitrogen above the value of 14° API gravity for the feed oil. The viscosity reduction and conversion of hydrocarbons with boiling point 343 °C+ into lower boiling distillable fractions followed the same trend as the API gravity. The percentage loss in specific surface areas as a result of coke deposition in the different reaction gases were as follows: 57.2% for hydrogen, 68% for methane, and 96% for nitrogen relative to the surface area of the fresh catalyst of 214.4 m<sup>2</sup> g<sup>−1</sup>. It was found that the spent catalyst contained 6 and 3 wt.% less coke after six hours operation when using hydrogen and methane reaction gases respectively compared to 23.5 wt.% coke content in a nitrogen atmosphere. Also, 48.5% of the catalyst specific surface area was recovered after oxidative regeneration.

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## 1. Introduction

The International Energy Agency (IEA) [1] has forecast 40% growth in worldwide primary energy resources demand by 2035. The same report shows that among fossil fuels, crude oil accounts for 32% of world energy demand which is likely to remain the

principal energy source for at least the next two decades. However, conventional light oils characterised by low viscosity, high API gravity, and low hetero-atom (e.g., S, N, Ni, V) content currently make up most of the crude supplied globally [2]. Peak production of conventional light oil is likely to occur before 2035 [1,3], thereafter a decline in supply will occur if alternative sources are not found and exploited. The vast deposits of heavy oil and bitumen, especially in Canada and Venezuela, make up approximately 80% of the world's remaining reserves which will need to be exploited at an accelerated pace to offset the decline in production of conventional oils [4].

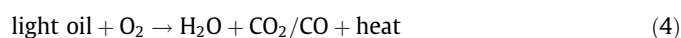
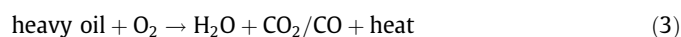
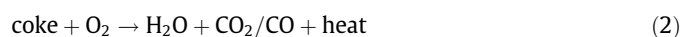
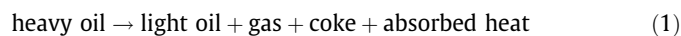
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Heavy oil and bitumen cannot be refined by conventional refineries without upgrading processes to convert them to synthetic light crude oil first in order to meet the required refinery feedstock specification [5]. The necessary upgrading of heavy oil and bitumen adds to the cost of their exploitation through the transport of oil, construction and operation of upgrading facilities [6]. Surface upgrading is conventionally used, although in situ upgrading provides the possibility of improving the oil properties before it is produced from the well. Surface upgrading technologies include coking, thermal and/or catalytic cracking, visbreaking, and hydro-conversion processes [7]. The coking process accounts for the production of roughly 30 wt.% of the heavy oil, but suffers from disadvantages in terms of handling the coke stockpiles generated and subsequent lower liquid yield [8]. Hydroconversion not only upgrades the heavy crude oil, but also produces a high yield of liquid synthetic crude with lower impurities, such as sulphur, nitrogen, and metals [9,10]. This is because the addition of hydrogen can offer alternative reaction pathways, by means of inhibiting the dehydrogenation reactions and lowering the amount of coke precursors in the reaction media, resulting in less coke formation and high liquid yield [11]. However, it is known that hydrogen and methyl radicals are sources of the smallest radicals found in the reaction media that can quench free radical addition reactions, which if not terminated would otherwise lead to the formation of larger molecules and coke. In fact, methane has the highest  $H/C$  ratio among the hydrocarbons, making it a potential alternative to expensive hydrogen gas as a source of hydrogen atom in the reaction medium.

In situ upgrading technologies offer some environmental advantages, because unwanted contaminants of the heavy oil are retained in the reservoir. THAI–CAPRI is a fairly new technology which involves simultaneous thermal enhanced oil recovery combined with down-hole in situ catalytic upgrading of the mobilized heavy oil to light oil [12–15]. As the combustion front moves forward from the toe position of the horizontal producer well to the heel, coke lay-down occurs, with the deposited coke being subsequently burnt to sustain the combustion process. The resulting heat causes oil ahead of the coke zone to flow towards the horizontal well in a region known as the mobile oil zone (MOZ). The following combustion reactions generate gases as illustrated by the following four equations [13–16]:



These reactions aid the thermal upgrading of the heavy oil; light oil is first generated as shown in Eq. (1) and the other reactions generate heat to drive the reaction. In the CAPRI ‘add-on’ to THAI, the hot oil flows downward by gravity through the catalyst layer packed in an annulus around the horizontal production wellbore and further upgrading occurs by catalytic conversion into light oil.

The CAPRI process has been previously investigated by the authors using a set of micro-reactors to replicate underground upgrading conditions and to optimise the selection of catalyst type, oil and gas flowrate, reaction temperature and pressure [17]. They concluded that the potential of the technology can be limited by the deposition of asphaltenes, coke and metal, which drastically deactivates the catalyst. Recently, Hart et al. [15] reported the use of activated carbon as a guard bed to filter out some of the macromolecular coke precursors prior to catalytic cracking and the addition of hydrogen to the feed in order to reduce deactivation resulting from coke lay-down. In the present study, the effect of the

type of reaction gas upon the extent of upgrading and coke formation upon the catalyst of the CAPRI section was investigated. In particular the use of hydrogen, methane, nitrogen, and a blended THAI gas mixture were studied over a Co–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at a previously determined optimum process reaction temperature of 425 °C, pressure 20 bar, oil flow 1 mL min<sup>−1</sup>, and gas-to-oil ratio 500 mL mL<sup>−1</sup>.

## 2. Materials and methods

### 2.1. Feedstock and catalyst

The heavy crude oil was supplied by Petrobank Energy and Resources Ltd. from its WHITESANDS THAI Pilot trial at Christina Lake, Alberta, Canada. The feedstock consisted of blended oil from eight different wells partially upgraded by THAI field trials; the physical and chemical properties of the feedstock are presented in Table 1. The properties of the Co–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst have been reported elsewhere [15].

### 2.2. Experimental apparatus

The micro-reactors used in this study to experimentally simulate the down-hole CAPRI reactor have been described in detail elsewhere [15,17]. Briefly, the micro-reactors each consist of a fixed catalytic bed of 1 cm diameter and length 41 cm. The reactors have three distinct zones: pre-heating, catalyst bed and post reaction zones. The first zone was packed with inert glass beads 3 mm in diameter to a length of 9.3 cm to ensure homogeneous flow distribution of the feed oil and gas, to enhance the radial contact and prevent axial mixing. The middle zone contains the catalyst bed comprised of 6 g of Co–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst pellets (diameter 0.14 cm and length 0.571 ± 0.293 cm), with a volume of 9.11 cm<sup>3</sup>. This section is intended to represent a cylindrical core of 1 cm diameter and 11.6 cm height taken in the radial direction of the annular CAPRI section of the well. Finally, the post reaction zone of the reactor was also packed with an inert glass beads to facilitate the disengagement of the gas–oil mixture by the impingement of oil droplets upon the beads. The experimental setup was built and commissioned at the School of Chemical Engineering, University of Birmingham, UK. The operating conditions of the experiments are presented in Table 2. In order to understand the influence of the generated gases of the THAI process on the CAPRI upgrading effect, a laboratory bottled gas mixture representing the typical combustion gases released by in situ combustion in the THAI process, consisting of 13% CO<sub>2</sub>, 3% CO, 4% CH<sub>4</sub>, and 80% N<sub>2</sub>, was used as gas feed in selected experiments.

**Table 1**  
Properties of the THAI feed oil.

Property	Value
API gravity (°)	14.1
Viscosity at 20 °C (Pa s)	1.091
Density at 15 °C (g cm <sup>−3</sup> )	0.972
Sulphur (wt.%)	3.52
Nickel (ppm)	41
Vanadium (ppm)	108
Ni + V (ppm)	149
Asphaltene (wt.%)	10.4
ASTM D2887 distillation (°C)	
10 (vol.%)	177
300 (vol.%)	271
50 (vol.%)	325
70 (vol.%)	375
90 (vol.%)	440

**Table 2**  
Operating conditions in the experiments.

Parameter	Value
Feed oil flow rate (mL min <sup>-1</sup> )	1
Catalyst mass (g)	6
Pressure (bar g)	10
Reaction temperature (°C)	425
WHSV (h <sup>-1</sup> )	9
Gas-to-oil ratio (mL mL <sup>-1</sup> )	50

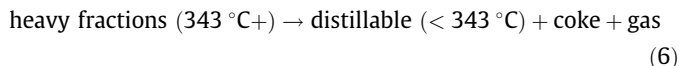
In selected experiments the catalyst was reduced with hydrogen prior to the experiments at 425 °C for 45 min. The catalysts used for the experiments were industrial hydroprocessing catalysts. When starting up the reactor, the feed lines and furnace were pre-heated under a flow of nitrogen/hydrogen/methane or THAI gas depending on the reaction gas in use. The oil flow was started once the temperature and pressure reached the desired values in the reactor bed for a particular experiment and the trace heating surrounding the oil lines reached its set point. All experiments were terminated by first stopping the oil flow and then turning off the heating followed by the gas flow. Liquid samples were withdrawn at regular intervals for analysis. Gas analysis was carried out periodically for particular runs.

### 2.3. Analysis of products

The API gravities of the feed and produced oils were measured using an Anton Parr DMA 35 portable density meter (Anton Paar GmbH, Austria) at 15 °C. The change in API gravity was calculated using Eq. (5):

$$\text{Change in API gravity (}^\circ\text{)} = \text{API of feedstock} - \text{API of produced oil} \quad (5)$$

Method ASTM-D2887 provides a comprehensive boiling range distribution of carbon numbers of petroleum and its distillates. For this reason simulated distillation (SIMDIS) based on an Agilent 6850N GC and calibrated in accordance with the ASTM-D2887 was used to characterize the feed and produced oils. The Agilent 6850N Network gas chromatograph system was fitted with a J&W 125-10 DB-1 10 m length, 530 µm ID and 2.65 µm film thickness capillary column. Prior to the injection of the sample, the feed and produced oil samples were diluted with carbon disulphide (CS<sub>2</sub>) in a ratio of 1:10. The percentage conversion of high-boiling-point (or high molecular weight) fractions to lighter fractions (boiling less than 343 °C) was defined as the conversion of the 343 °C+ hydrocarbons (HCs) that are found in the THAI feed oil to the produced upgraded oils. The chemical reactions for the conversion of the heavy fractions by thermal and catalytic cracking during CAPRI can simply be expressed by Eq. (6):



The distillables consist of light and medium oil fractions in the produced oil. Therefore, the calculation was made by first determining the weight of the 343 °C+ HCs in the THAI feed oil and the liquid products, then using Eq. (7) to calculate the conversion.

$$\text{Conversion} = \frac{(343\text{ }^\circ\text{C+})\text{HC in feed} - (343\text{ }^\circ\text{C})\text{HC in products}}{(343\text{ }^\circ\text{C})\text{HC in feed}} \quad (7)$$

The advanced rheometer AR 1000 (TA Instruments Ltd, United Kingdom) was used to measure the viscosity of the THAI feed oil and produced oils. All viscosity measurements were performed at 20 ± 0.1 °C. An aluminium plate of parallel geometry with diameter

40 mm and a polished surface was used. The parallel plate gap size was set at 150 µm and a shear rate of 100 s<sup>-1</sup> was used for all measurements. The extent of viscosity reduction was calculated using Eq. (8):

$$\text{Viscosity reduction (\%)} = (\mu_o - \mu) / \mu_o \times 100 \quad (8)$$

where  $\mu_o$  and  $\mu$  viscosity of the THAI feed oil and produced oil (Pa s), respectively.

The gas products were analysed using an Agilent 7890A Refinery Gas Analyser (RGA) to determine the volume percentage of H<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>1</sub>–C<sub>5</sub> hydrocarbons. The three channels of the RGA include a flame ionization detector (FID) and two thermal conductivity detectors (TCD). The light hydrocarbon components in the gas stream were determined by the FID channel column HP-PLOT Al<sub>2</sub>O<sub>3</sub>S, which is capable of separating C<sub>1</sub>–C<sub>5</sub> including their 22 isomers based on the calibrated table, whilst components heavier than nC<sub>6</sub> are back flushed through the pre-column. One of the TCDs operates with helium carrier gas and is used to analyze for permanent gases such as N<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>S. The other TCD with nitrogen as carrier gas determines the quantity of gases such as hydrogen and helium. The oven column dimension is 27 m × 320 µm × 8 µm and the column operates at a temperature of 200 °C. The RGA takes 15 min to complete the analysis of one gas sample.

A thermogravimetric analyser (TGA) was used to determine the amount of coke deposit on the spent catalysts. In this study, TGA was carried out with a NETZSCH-Geratebau GmbH, TG 209 F1 Iris® instrument. A mass of 16–17 mg of the spent catalyst sample was recovered from the centre of the catalyst bed and placed on platinum crucible above the microbalance. The micro-furnace was programmed as follows: firstly a linear temperature ramp over the range of 25–900 °C at a heating rate of 10 °C min<sup>-1</sup> was performed under air environment with flow rate of 50 mL min<sup>-1</sup>. At 900 °C an isothermal condition was maintained for 20 min to enable total burn-off of the materials deposited on the spent catalysts. The total time for each run is 1 h 47 min and the air flow rate during the TG analysis was set at 50 mL min<sup>-1</sup>.

The asphaltenes fraction of the heavy oil may be recovered by dilution with straight chain alkanes such as n-pentane or n-heptane and recovering the precipitate obtained. The remaining portion thereafter is known as maltene, which consists of a mixture of saturates, aromatics, and resins. In this study, the asphaltene fraction was precipitated from the corresponding THAI feed oils and produced upgraded oils using n-heptane in accordance to the ASTM D2007-80. Specifically, 1 g of the samples was mixed with 40 mL volume of n-heptane, as a precipitant. The mixture of oil and n-heptane was agitated for 4 h using a magnetic stirrer. Thereafter, the mixture was left for 24 h to allow the asphaltenes to precipitate and settle. The precipitated fraction was collected and vacuum filtered using a Whatman 1 filter paper with 11 µm pore size and 4.25 cm diameter to separate the n-heptane soluble portion (i.e., maltene) from the asphaltene portion (i.e., n-heptane insoluble). The filtered asphaltenes were washed with n-heptane until a colourless liquid was observed from the filter. The filter paper and precipitate were dried under an inert gas flow for 24 h to remove any residual n-heptane, and then the precipitated asphaltenes were weighed.

The spent catalyst from upgrading reaction with nitrogen atmosphere was regenerated at high temperature using 14.4 g of the spent catalyst in a Carbolite® furnace (Keison Products, UK) under air atmosphere, thereafter reduction was performed in the CAPRI reactor using hydrogen gas at a flow rate of 50 mL min<sup>-1</sup> for 45 min, before being retested for catalytic activity. The furnace was programmed as follows: ramp increase in temperature in range of 25–600 °C at a heating rate of 20 °C min<sup>-1</sup>, followed by holding the temperature at 600 °C for a total of four hours to avoid



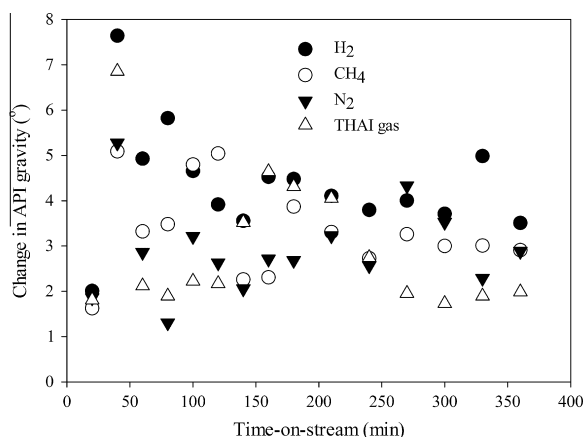
sintering. This temperature is typical of the regeneration temperature used in fluidised bed catalytic cracker reactors in the petroleum industry. At the end of the reaction, 24.5 wt.% of the carbonaceous deposits were burned-off upon thermal regeneration. Nonetheless, this oxidative-regeneration removes mostly the asphaltene and coke deposits, whilst the metal sulphides of Mo and Co are transformed into their oxides, which was reduced with hydrogen before reuse. The regeneration therefore does not remove the metal deposits.

### 3. Results and discussion

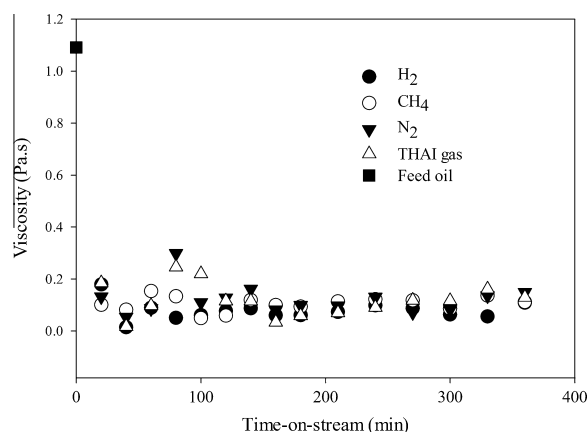
Upgrading results are presented below for experiments carried out under hydrogen, methane, THAI gas and nitrogen reaction environments. Methane could provide a potential alternative to expensive hydrogen for injection into the well. These sets of experimental runs were conducted at a reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil ratio 50 mL mL<sup>-1</sup> for 6 h time-on-stream operation.

#### 3.1. Effect reaction media upon API gravity

The reported data points on the graphs are average values taken from duplicate experimental runs with mean standard deviation of  $\pm 0.41^\circ$  API. The change in API gravity of the produced upgraded oils as a function of time-on-stream are respectively shown in Fig. 1 for hydrogen, methane, THAI gas, and nitrogen reaction gas. The feed oil had an API gravity of 14°. Upon processing in hydrogen, the initial change in API gravity for the first sample taken from the reactor at 25 min was quite low, before increasing up to a maximum of 8° points after 50 min, thereafter decreasing and settling at an average of  $4.4 \pm 1.3^\circ$  increase in API points. Similarly for reaction in methane the increase in API gravity was initially 5° thereafter settling at an average of  $3.33 \pm 1.02^\circ$  API, whilst for THAI gas the initial upgrading was 6.9° settling at an average increase of  $2.93 \pm 1.47^\circ$  API. For nitrogen the maximum upgrading of 5° occurred thereafter settling at an average increase of  $2.72 \pm 1.02^\circ$  API. A possible reason for the low API gravity change of the first sample taken from the reactor could be instability of oil flow at start up due to the difficulties of regulating the flow manually using a metering valve. Secondly, the catalyst may not have been fully activated at the start of the reaction.



**Fig. 1.** Change in API gravity of the produced upgraded oils as a function of time-on-stream for hydrogen, methane, THAI gas and nitrogen reaction gas media at temperature of 425 °C, pressure 10 bar, and gas-to-oil 50 mL mL<sup>-1</sup> using Co–Mo catalyst.



**Fig. 2.** Viscosity of the produced upgraded oils as a function of time-on-stream for hydrogen, methane, THAI gas and nitrogen reaction gas media at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil 50 mL mL<sup>-1</sup> using Co–Mo catalyst.

#### 3.2. Effect reaction media upon viscosity

Viscosity is an important physical property of the crude oil and as a guideline should be lower than 0.2 Pa s at 20 °C to achieve pumping in pipeline transport [18]. In Fig. 2, the viscosity of produced upgraded oil samples as a function of time-on-stream under the different reaction gas media are presented. The viscosity reduced from the feed value of 1.091 to 0.078 Pa s (92.8% reduction) in hydrogen, reduced by 0.105 Pa s (90.4% reduction) in methane and by 0.1181 Pa s (89.2% reduction) in THAI gas blend. An upgrading experiment carried out under nitrogen as an inert or control experiment led to oil with lowest change in API gravity of 2.71° and smallest viscosity reduction of 0.121 Pa s (88.9% reduction).

Comparing upgrading performance of the different gases, the biggest change in API gravity of an additional 1.68° and viscosity reduction of 3.9% occurred under hydrogen as compared with the values under nitrogen, suggesting that hydrogen participated in further upgrading reactions. The produced oil under methane also showed additional upgrading, with a further increase of 0.44° API and 1.5% viscosity reduction occurring under methane compared with nitrogen. From the above results (see Figs. 1 and 2) it appears that there was no significant difference in API gravity and viscosity of produced oil upon the use of THAI gas, with API gravity increase of 0.21° and average viscosity reduction 0.3%, from oils upgraded under nitrogen. The slight improvement in API gravity and viscosity under THAI gas above that of nitrogen can be attributed to the activity of 4% methane in the THAI gas, which may provide a hydrogen source to assist the upgrading reactions.

#### 3.3. Effect reaction media upon yield of distillable

The simulated distillation method was found to be suitable for analysing oil within the carbon range C<sub>5</sub>–C<sub>50</sub>. In Fig. 3, the true boiling point (TBP) distribution curves for the feed oil and the produced oils upgraded under hydrogen, methane, THAI gas, and nitrogen reaction media are presented. It is clear that the yield of distillate (i.e., low boiling fractions) increased above that of the feed oil for all the experimental runs as indicated by the shift of the distillation curves to the left of the feed oil curve. However, the distillables increased further upon the addition of hydrogen and a slight increase was also observed with that of methane compared to the use of THAI gas and nitrogen in relation to the feed oil. The improvement upon hydrogen addition is in line with the reports of Hart et al. [15] and Longstaff et al. [10].

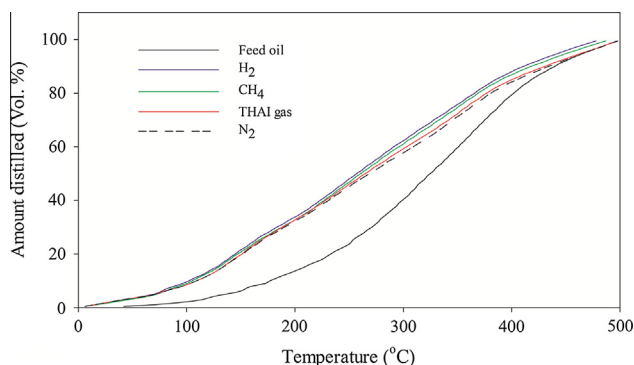
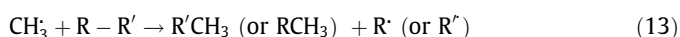
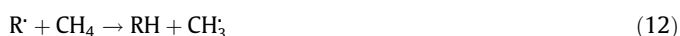
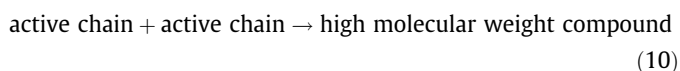
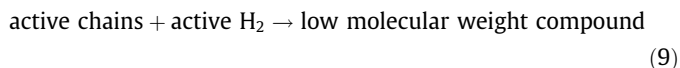


Fig. 3. TBP distribution curves for the feed oil and the produced upgraded oils under hydrogen, methane, THAI gas and nitrogen reaction environment at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil 50 mL mL<sup>-1</sup> using Co–Mo catalyst.

The conversions of 343 °C+ HC fractions under hydrogen, methane, THAI gas, and nitrogen atmospheres compared to 343 °C– HC fractions were 41%, 38.1%, 32.6% and 29.5%, respectively. These values follow the trends observed in Fig. 3, and also reflect similar results observed for the API gravity and viscosity presented in Figs. 1 and 2, thus confirming that hydrogen and methane are involved in the upgrading reactions. The increased distillable fractions (343 °C–) of the produced oil in hydrogen and methane are thought to be mainly due to the minimisation of retrogressive polymerisation reactions occurring in the upgrading process, compared with the macromolecular radical addition reaction to form high boiling fractions observed with inert nitrogen. These hydrogen donor reaction mechanisms are thought to be responsible for the increased yield of light and middle hydrocarbon distillates [19]. Ancheyta et al. [18] pointed out that the viscosity of the oil depends on the amount of the >350 °C heavy fractions and/or the yield of <350 °C distillates fractions. Therefore, increased conversion of 343 °C+ fractions to lower boiling range through treatment in the CAPRI process could potentially achieve a remarkable reduction in oil viscosity, improving its pump-ability. This is because increased lighter fractions in the produced oil thin the unconverted heavy fractions and result in significantly lower viscosity, as reflected in Fig. 2.

As observed in Figs. 1–3, the CAPRI upgrading reactions conducted under hydrogen atmosphere produced oil with improved API gravity, viscosity and conversion of 343 °C+ fraction than the values obtained under methane, followed by THAI gas and nitrogen. Hence, the order of reactivity of these gases during upgrading reaction may be summarised as H<sub>2</sub> > CH<sub>4</sub> > THAI gas > N<sub>2</sub>, which is consistent with the reports of Ovalles et al. [20,21]. The termination of free radical addition reactions in hydrogen atmosphere, shown in Eqs. (9) and (10), may have contributed to these improvements. Also, the free-radical pathway that occurs in methane during upgrading reactions (Eqs. (11)–(13)) is thought to be a mechanism by which the API gravity and viscosity of the oil are improved [20].



where R and R' are naphthenic or aromatic hydrocarbons.

Methane can be catalytically activated and also become involved in heavy oil upgrading reactions due to hydrogen abstraction by cracked fragments of hydrocarbon molecules to produce methyl radicals. In turn these react with hydrocarbon molecules producing methylated species (RCH<sub>3</sub>) and further free radicals (R<sup>•</sup>) in a continuous chain process, as illustrated in Eqs. (11)–(13) above [20]. Ovalles et al. [20] studied the mechanism of methane activation using MoS<sub>2</sub> catalyst and methane at a reaction temperature of 420 °C and pressure of 0.3 MPa. They found that the methane decomposes to form CH<sub>x</sub> (where x = 1, 2, or 3) and H<sub>4–x</sub> species on the surface of catalyst, with an abundance of methyl (CH<sub>3</sub>) species all attached to the catalyst surface. The adsorbed CH<sub>x</sub> on the catalyst surface can be incorporated into the hydrocarbon molecules to form methylated products, and subsequently the H<sub>4–x</sub> species are available to hydrogenate cracked fragments, acts as coke precursors and remove sulphur in the form of H<sub>2</sub>S [21].

In terms of thermal upgrading, the most fundamental cleavage reaction in heavy oil upgrading is the temperature driven splitting of C–C bonds. This can lead to remarkable molecular weight reduction, notable increase in distillable fractions, significant viscosity reduction, and change in API gravity. In the previous work of Hart et al. [15] with nitrogen gas media at 350, 400 and 425 °C the average changes in API gravities were respectively 2, 2.8, and 3.7° API, viscosity reductions were 42%, 65.3% and 81% and conversions of boiling fractions >343 °C were 16.5%, 28.6% and 36.5%. In this work improvements in the API gravity, viscosity, and the distillable yield upon upgrading with methane, THAI gas and nitrogen only vary within a relatively narrow range but slightly higher differences are observed for reactions performed with hydrogen (Figs. 1–3). This confirms that the primary upgrading reactions depend mostly on the reaction temperature, whereas the reaction media play a role in the chemistry of upgrading reactions.

### 3.4. Effect on produced gas composition

The composition of the outlet gas during CAPRI reaction tests under hydrogen, methane, THAI gas, and nitrogen atmospheres are presented in Table 3, from which it can be observed that the outlet gas stream consists of paraffin and olefin hydrocarbons. Olefins are known coke precursors because they can transform into larger molecular weight compounds if there is insufficient active hydrogen available to quench their addition reaction. From Table 3, the total paraffin content of the gas under hydrogen and nitrogen atmosphere are 9.23 and 6.67 vol.%, respectively. The olefin contents for the produced gases upon upgrading under the following feed gases were: hydrogen (0.81 vol.%), methane (0.86 vol.%), THAI gas (1.1 vol.%), and nitrogen (1.24 vol.%). Moreover, the amount of olefins in the off-gas upon the use of THAI gas was 0.14 vol.% less than that of nitrogen used in the inert control run. It was deduced that the amounts of ethene, propene, trans-2-butene, and cis-2-butene decreased upon the use of hydrogen and methane as reaction media compared to the use of THAI and nitrogen gases. This shows that hydrogen and methane are involved in the reaction and the addition of hydrogen promotes hydrogenation of olefins to paraffins, which was further confirmed by a corresponding increase in the amount of paraffins in the outlet gas. Under a hydrogen environment, the generated methyl radicals during upgrading reactions may have been terminated by hydrogen which gave rise to the increased amount of methane gas in the outlet gas stream compared to nitrogen atmosphere.

Table 3 shows that the produced hydrogen sulphide under hydrogen atmosphere is respectively 1.4 and 2.8 times the values obtained under methane and nitrogen gas reaction media. This provides evidence that hydrodesulphurisation (HDS) reactions occurred to a greater extent under hydrogen reaction media

**Table 3**Outlet Gas composition for different reaction gas media; temperature 425 °C, pressure 10 bar, gas-to-oil ratio 50 mL mL<sup>-1</sup>.

Gas composition	Hydrogen (vol.%)	Methane (vol.%)	THAI gas (vol.%)	Nitrogen (vol.%)
Methane	5.93	78.08	10.5	2.3
Ethane	0.37	0.49	0.35	0.47
Ethene	0.19	0.21	0.31	0.29
Propane	1.21	2.37	1.63	2.06
Propene	0.37	0.39	0.41	0.58
n-Butane	0.52	1.02	0.79	0.82
i-Butane	0.54	0.38	0.21	0.34
1-Butene	0.13	0.13	0.18	0.18
Trans-2-butene	0.1	0.09	0.14	0.14
Cis-2-butene	0.03	0.04	0.06	0.05
i-Pentane	0.29	0.36	0.34	0.37
n-Pentane	0.37	0.45	0.49	0.37
Hydrogen	80.8	14.76	4.41	6.22
Hydrogen sulphide	0.001	0.00073	0.00063	0.00036
Carbon dioxide	0.11	0.1	6.36	0.68
Carbon monoxide	0.12	0.15	1.45	0.15
Total paraffin	9.23	5.07	3.81	6.67
Total olefin	0.81	0.86	1.1	1.24

Note: The methane component of the outlet gas stream was not included in the calculation of total paraffin under methane and THAI gas due to its initial presence in the gas.

compared to methane, THAI gas, and nitrogen. Additionally, the produced H<sub>2</sub>S under methane and THAI gas atmosphere were 2 and 1.75 times that produced when nitrogen gas was used. This indicates that the generated active hydrogen from catalytic decomposition of methane can be partly consumed by hydrodesulphurisation, resulting in additional H<sub>2</sub>S in the released gas. It should be noted that the higher concentrations of CO<sub>2</sub>, CO and CH<sub>4</sub> in the gas under THAI gas atmosphere compared to the other reaction media are because of their presence in the feed (see Section 2.2).

### 3.5. Effect on asphaltenes, metals and sulphur content

The asphaltene, sulphur and metals contents of the feed and produced oils under the different reaction media are presented in Table 4. The asphaltene content decreased remarkably after CAPRI upgrading in the different reaction media relative to the feed oil. This suggests that the conversion of the heaviest fraction (asphaltene) to lighter fractions such as maltene, gases, and coke occurred. However, the use of hydrogen and methane produced higher conversions of asphaltene of 43.4 and 51.6%, respectively, compared to 13% in only nitrogen. This is concluded to be because the generated active hydrogen in hydrogen and methane media neutralised the cross-linking of macromolecular radical intermediates that are generated during cracking of the heavy oil [22]. Conversely, the

asphaltene content of the produced oil upon the use of methane is lower than that of hydrogen. This can be attributed to the larger amount of dissolved hydrogen under an atmosphere of pure hydrogen at 10 bar compared with the low partial pressure of generated hydrogen from methane. The increased hydrogen dissolved in the oil with the hydrogen feed was assumed to promote condensation reactions between radicals of asphaltene macromolecules [22].

One of the objectives of upgrading is to remove impurities such as metals and sulphur to a level that will minimise their impact on downstream processing catalysts and equipment and also improve the yield of light end distillates. The results show that in all cases the sulphur and metals content of the produced oil in different reaction media were less than those of the feed oil, which indicates that the Co–Mo/alumina HDT catalyst was active for desulphurization and demetalization reactions. It was therefore deduced that the breaking of C-heteroatom bonds in addition to C–C bond cleavage contributed to the increased change in API gravity, decreased viscosity, and improved yield of distillates noticed in the produced oils. However, when hydrogen gas was used as reaction gas medium, sulphur removal was 21.4%, which is significantly higher than the values obtained using methane (12.2%) and nitrogen (3.4%). Some of the sulphur content is removed in gaseous form as H<sub>2</sub>S, which was confirmed by the high concentration of hydrogen sulphide detected in the product gas when hydrogen feed was used. This is because the hydrodesulphurisation (HDS) reaction was promoted in the presence of hydrogen, which was not experienced to the same extent in the methane and inert nitrogen atmospheres.

It can be seen from Table 4 that the cracking of asphaltenes resulted in a decrease in sulphur and metal content in the produced oil. This suggests that sulphur and metals such as nickel and vanadium in porphyrin-like form, were associated with asphaltene molecules [23]. The percentage reductions of nickel plus vanadium (Ni + V) content under the different environments were: 16.8% for a nitrogen atmosphere, 26.9% for methane and 16.2% for hydrogen from the value for the feed oil of 149 ppm. This observed behaviour can be attributed to the conversion of asphaltenes into smaller molecules in the different environments as shown in Table 4. Under the same conditions other trace elements such as boron, iron, and silicon were reduced after upgrading. These metals are transformed into metal sulphides and deposited on the catalyst causing deactivation by blocking catalyst pore mouth and poisoning active sites [23]. This suggests that catalyst high activity should be harmonized with high metal tolerance.

**Table 4**

Asphaltene, metals, and sulphur content before and after CAPRI reaction using Co–Mo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst under hydrogen, methane, THAI gas, and nitrogen atmospheres at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil ratio 50 mL mL<sup>-1</sup>.

Impurities	Feedstock	N <sub>2</sub>	CH <sub>4</sub>	THAI gas	H <sub>2</sub>
Asphaltene (wt.%)	10.3	9.2	5.3	8.4	6.1
Aluminium (ppm)	2	2	2	N/A	2
Boron (ppm)	3	2	2		2
Iron (ppm)	5	2	<1		<1
Sulphur (wt.%)	3.52	3.4	3.09		2.77
Silicon (ppm)	1	<1	<1		<1
Nickel (ppm)	41	34	30		36
Vanadium (ppm)	108	90	79		89
Ni + V (ppm)	149	124	109		125

Sulphur and metals content was performed by Intertek Laboratories, Sunbury Technology Centre, UK, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). Sulphur and metals analysis were not performed for the use of THAI gas because the upgrading effect falls between the used of methane and nitrogen gas.

### 3.6. Effect on spent catalyst coke content

Coke formation is an inevitable by-product during catalytic upgrading of heavy crude oil. Its deposition decreases catalyst activity, and can be determined as the weight percent of coke on the catalyst [24]. The term coke is used to describe a carbonaceous material of reasonably low hydrogen content [25]. The spent Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts reacted under hydrogen, methane, THAI gas and nitrogen environments were analysed using TGA, the TG and DTG curves as presented in Fig. 4. The weight loss at the start of first peak around 200 °C is for the soft coke on the catalyst, whilst the weight loss from the start of the peak around 526 °C (see DTG curves) is sharp and prominent, and signified the start of hard coke burn-off. The coke contents of the spent catalysts under the different reaction media are presented in Table 5. It can be observed that the coke content of the spent catalyst after 6 h operation when reacted under a hydrogen atmosphere was lower than those of methane, THAI gas, and nitrogen at the same reaction conditions. The spent catalyst coke contents reacted under hydrogen, methane, and THAI gas were respectively 6, 3.1 and 2.7 wt.% lower than that obtained upon the use of nitrogen reaction media (23.5 wt.%). This implies that hydrogen and methane in the reacting media were involved in the upgrading reactions, hence most of the upgrading in nitrogen media can be attributed largely to carbon-rejection with a low degree of hydrogenation occurring [15].

During the CAPRI process, most of the C–C bond cleavages take place through a free radical mechanism described above, in which thermal cracking forms distillable fractions with lower molecular weight; the asphaltene molecules lose their paraffin side chains through de-alkylation reactions and in the process large aromatic radicals are produced [22,26,27]. The off-gas composition shows the substantial presence of hydrogen, C<sub>1</sub> and C<sub>2</sub> gases, from which hydrogen, methyl, and ethyl reactive radicals may form in the reaction media. The concentrations of these radicals in oil being processed are related to the gas phase composition by an equilibrium relationship. The subtraction of hydrogen rich components such as hydrogen, methane, and ethane by the gas phase radicals from the polymerised oil and coke precursor molecules are therefore a potential contributor to the growth of coke lay-down on the catalyst. The active hydrogen and methyl species in hydrogen, methane and THAI gas reaction gas media are thought to suppress the addition reactions of coke precursors, and cause less coke formation because they subsequently inhibit the dehydrogenation reaction occurring after the condensation of poly-aromatics. On the other hand, in inert nitrogen gas, these large radicals cross-link together, condense and finally form coke through hydrogen

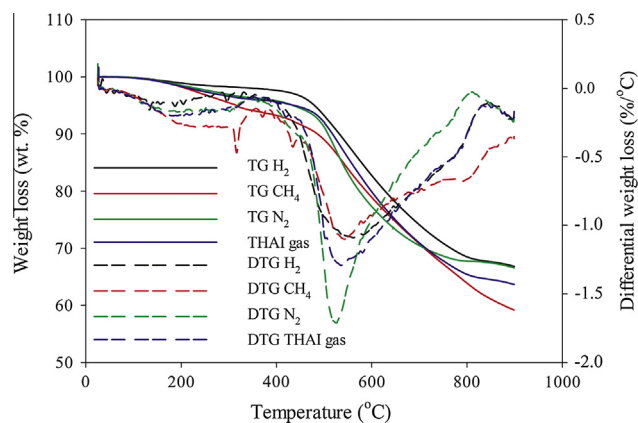


Fig. 4. TG and DTG of spent Co-Mo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst after 6 h time-on-stream reaction under hydrogen, methane, THAI gas, and nitrogen atmospheres at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil ratio 50 mL mL<sup>-1</sup>.

Table 5

Coke content of spent Co-Mo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst under hydrogen, methane, THAI gas and nitrogen atmospheres at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil ratio 50 mL mL<sup>-1</sup>.

Reactants	Spent catalyst coke content (wt.%)
Heavy oil + H <sub>2</sub>	17.4 ± 0.82
Heavy oil + CH <sub>4</sub>	20.4 ± 1.32
Heavy oil + THAI gas	20.08 ± 0.97
Heavy oil + N <sub>2</sub>	23.5 ± 1.06

subtraction. Under hydrogen and methane, the produced large aromatic radicals are terminated by released active hydrogen and methyl suppressing coke formation [22,26]. Consequently the coke content of the spent catalyst under methane atmosphere is notably lower than that reacted under nitrogen (see Table 5).

Deactivation of a catalyst can occur by poisoning, aging, fouling and sintering; however the major cause of deactivation in CAPRI is thought to be the formation of coke. In the light of this, the nitrogen adsorption–desorption isotherms for the fresh and spent Co-Mo catalyst recovered from the CAPRI reactor after 6 h upgrading in hydrogen, methane, and nitrogen gas media were determined and are presented in Fig. 5. The percentage loss in specific surface area in the different reaction media are as follows: 57.2% for hydrogen, 68% for methane, and 96% for nitrogen relative to the fresh catalyst with specific surface area 214.4 m<sup>2</sup> g<sup>-1</sup>. Note the nitrogen adsorption–desorption isotherm of the spent catalyst recovered after upgrading reaction with THAI gas contains a large amount of oil in both duplicate experimental runs which can create a vapour pressure and damage the Micromeritics Analytical Instrument ASAP® 2010 used. If dried externally the residual oil on the spent catalyst will add to surface area loss. However, Table 5 shows that the coke content of the spent catalyst with methane and THAI gas were approximately 20 wt.% compared to 23.5 wt.% with nitrogen. Therefore, the loss in specific surface area for THAI gas could be in the same range as that for methane gas.

Among several possible deactivation mechanisms such as sintering, active site coverage and poisoning, catalyst deactivation can also occur as a result of loss of surface area caused by coke deposition [28]. The surface areas are consistent with the coke contents of catalyst presented in Fig. 4, showing that hydrogen and methane are effective reactants during catalytic upgrading to reduce coke deposition in the catalyst pores compared to nitrogen. As the coke deposits increase inside the porous structure of the catalyst they retard its activity and lower conversion of 343 °C+

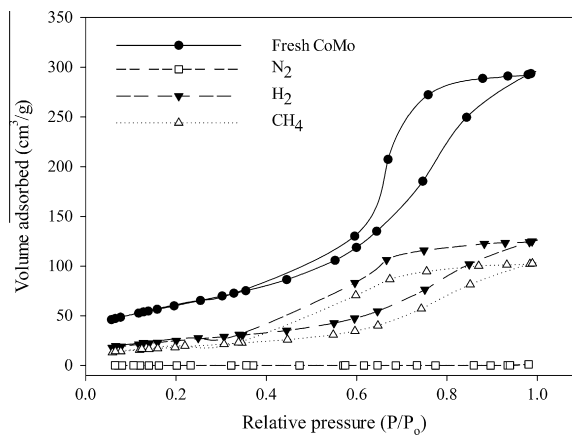


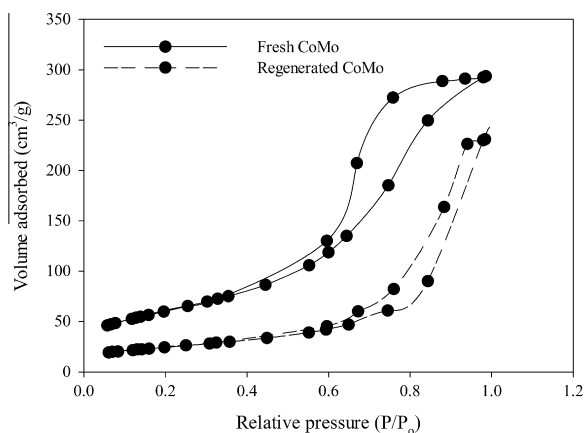
Fig. 5. Nitrogen adsorption–desorption isotherm of fresh and spent Co-Mo after 6 h reaction in hydrogen, methane, and nitrogen media at reaction temperature of 425 °C, pressure 10 bar, and gas-to-oil 10 mL mL<sup>-1</sup>.



hydrocarbon fractions. Gray et al. [28] pointed out the mechanism for the three stages of catalyst deactivation by coke are as follows: (1) rapid formation of initial coke with remarkable loss of catalytic activity; (2) gradual build-up of coke and metal deposits resulting in further loss of activity; and (3) pore blockage due to progressive deposition of coke and metals leading to loss of activity. Coke build up under nitrogen was higher than hydrogen, methane and THAI gas reaction media (Fig. 5), which is thought to be due to the inert nature of nitrogen which does not suppress poly-aromatics radical addition reactions. The losses in pore volume and surface area of the spent catalyst reacted in a nitrogen atmosphere are an indication of pore mouth plugging [15,23,29,30] caused by the deposition of asphaltenes and coke [15]. The small pores within the catalyst not only hinder access of macromolecules to the active sites but also are preferential sites for coke deposition, resulting in pore blockage and surface area loss [29]. Micro-structural properties of the catalyst support such as surface area and porosity, therefore determine to a certain degree the ability of the catalyst to adsorb asphaltene and coke deposits. The formation and deposition of coke limits the conversion of macromolecules to low boiling distillable liquid product.

### 3.7. Fresh vs. regenerated catalyst

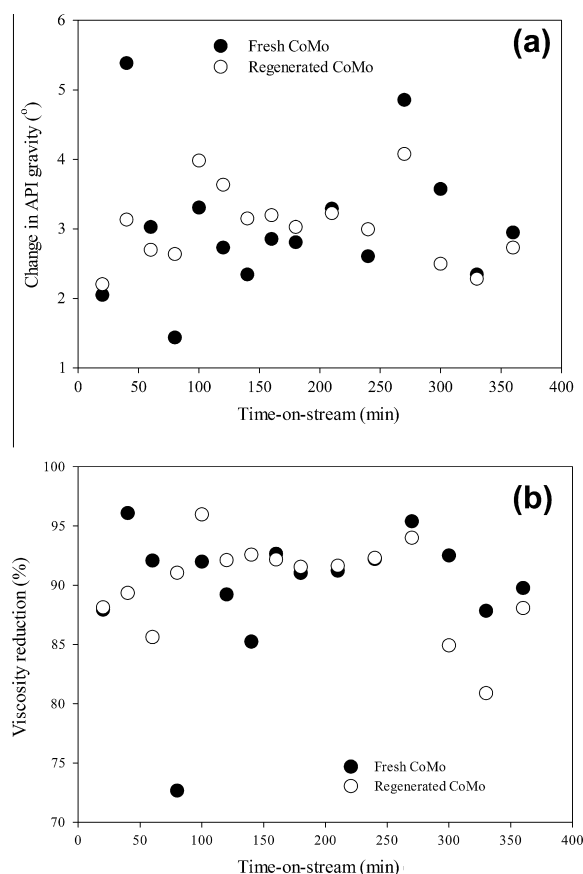
Oxidative-regeneration of spent catalyst could lead to lower catalyst costs, more favourable process economics and maximize utilisation of catalyst. Catalyst deactivation by coke is potentially reversible by burning-off the carbonaceous deposits in air at high temperature. It is well known that upgrading reactions occur on the catalyst surface [15], which needs to be recovered to restore catalyst activity. The nitrogen adsorption–desorption isotherms of the fresh Co–Mo catalyst and oxidative-regenerated spent Co–Mo catalyst from the nitrogen medium experiment are presented in Fig. 6. It is clear that the catalyst textural properties such as pore volume, specific surface area, and pore-size distribution changed after oxidative-regeneration in air environment at 600 °C relative to the fresh catalyst. This is mainly because of coke and metal deposits, which were not fully removed by the burning process. Additionally, the catalyst pore sizes became narrower with some of the micropores being blocked accompanied by a shift of the hysteresis loop towards higher relative pressure and lower adsorbed volume. From these data the specific surface area of the regenerated Co–Mo was calculated to be  $103.9 \text{ m}^2 \text{ g}^{-1}$ , which is lower than the value of  $214.4 \text{ m}^2 \text{ g}^{-1}$  for the fresh catalyst sample. This indicates that only 48.5% of the specific surface area was recovered after regeneration.



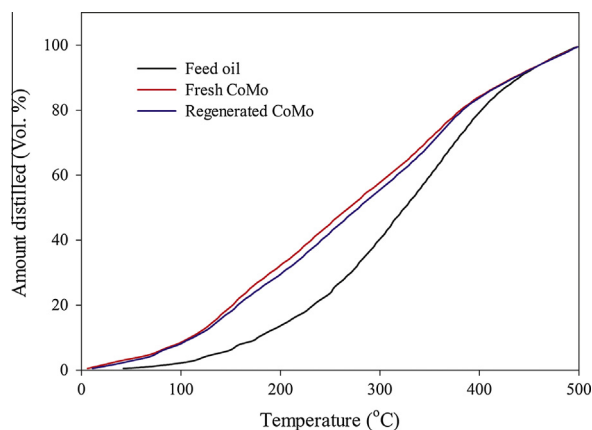
**Fig. 6.** Nitrogen adsorption–desorption isotherm of fresh Co–Mo catalyst and oxidative-regenerated spent Co–Mo catalyst from the nitrogen medium experiment.

The changes in API gravity and viscosity reduction between the produced and THAI feed oils for the fresh Co–Mo catalyst and the oxidative-regenerated spent Co–Mo catalyst from the nitrogen medium experiment are presented in Fig. 7(a) and (b) respectively, as a function of time-on-stream. The maximum change in API gravity for fresh Co–Mo catalyst was  $5.4^\circ \text{ API}$  compared with  $4.1^\circ \text{ API}$  for regenerated Co–Mo, but the average change in API gravity over the whole time on stream for both experimental runs settled at approximately  $3.04 \pm 1.01^\circ \text{ API}$ . The regenerated catalyst showed a similar level of activity over the whole time period of investigation compared with the fresh catalyst despite its loss of surface area. In Fig. 7 (b), there is no significant difference in the trend of viscosity reduction as a function of time-on-stream between the use of fresh and oxidative-regenerated Co–Mo catalyst. Notably, the average viscosity reduction in both runs was approximately 90%. This trend is consistent with that of the API gravity.

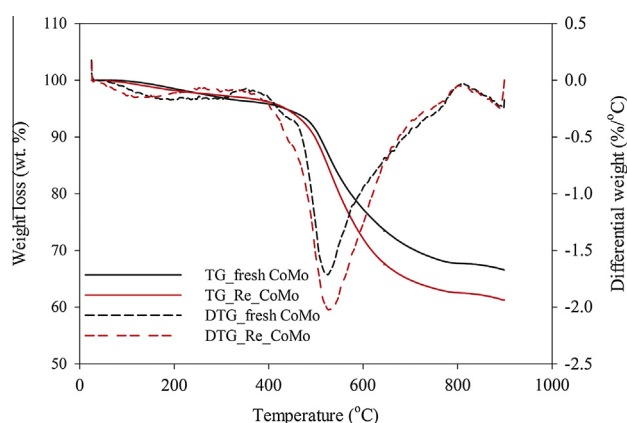
In Fig. 8, the simulated distillation curves for the feed and produced oils with fresh Co–Mo catalyst and regenerated spent Co–Mo from experiment performed under nitrogen reaction media are presented. It is clear from the curves that distillates in the produced oil from fresh Co–Mo were improved compared with regenerated Co–Mo. Conversion of 29.5% of  $343^\circ \text{C}+$  hydrocarbons from the feed oil into low boiling products occurred for the fresh Co–Mo and 25% for the regenerated Co–Mo catalysts, showing a further decrease of 4.5% after regeneration of the spent Co–Mo catalyst. This is concluded to be because some of the catalyst active sites may have been fouled and poisoned by coke and metal during the first experimental run, as the deposited coke and metals on the



**Fig. 7.** Change in API gravity (a) and degree of viscosity reduction (b) for the produced oil using fresh Co–Mo catalyst and oxidative-regenerated spent Co–Mo catalyst from the nitrogen medium experiment at reaction temperature of  $425^\circ \text{C}$ , pressure 10 bar, and nitrogen-to-oil ratio  $50 \text{ mL mL}^{-1}$ .



**Fig. 8.** TBP distribution curves for feed and upgraded oils obtained from using fresh Co–Mo catalyst and oxidative-regenerated spent Co–Mo catalyst from the nitrogen atmosphere experiment at reaction temperature of 425 °C, pressure 10 bar, and nitrogen-to-oil ratio 50 mL mL<sup>−1</sup>.



**Fig. 9.** TG and DTG curves of the spent Co–Mo catalyst obtained with the nitrogen reaction medium before and after oxidative-regenerated was conducted after 6 h time-on-stream reaction at temperature of 425 °C, pressure 10 bar, and nitrogen-to-oil ratio 50 mL mL<sup>−1</sup>.

spent catalyst were not completely removed by oxidative regeneration (see Fig. 6).

A comparison between the TG and DTG curves of the spent Co–Mo catalyst obtained with the nitrogen reaction medium before and after oxidative-regenerated was conducted and presented in Fig. 9 after 6 h time-on-stream experiment. The coke contents of the fresh and regenerated catalysts were 23.48% and 24.73%, respectively. It was noted that the coke content of the rejuvenated sample after reaction was 1.25% higher than the catalyst used only once, which indicates that regeneration promotes the propensity of the catalyst to support the formation of coke. The high yield of highly poly-aromatic coke corresponds to faster catalyst deactivation [14], with lower yield of liquid hydrocarbons of low boiling points upon the use of regenerated relative to fresh catalyst as reflected by the data shown in Fig. 8.

#### 4. Conclusions

The deposition of coke on the catalyst surface during the upgrading reactions in CAPRI is a major contributor to catalyst deactivation. It was found that the hydrogen and hydrogen donor reactive media play the role in inhibiting coke formation and growth, while also improving the quality and stability of produced

upgraded oil. The addition of hydrogen or a hydrogen donor to the feed promotes hydrocracking and hydrogenation reactions, whereas in a nitrogen atmosphere most of upgrading occurred via carbon-rejection with associated heavy coke deposition upon the catalyst. Macromolecular radicals formed from cracked oil molecules could be terminated by reaction with hydrogen or methane radicals, but continue growth by polymerisation under inert gases such as nitrogen. Hence, reaction under nitrogen leads to characteristically low API gravity, high viscosity, and low distillables in the produced oil compared with gases containing hydrogen and hydrogen-donor. Additionally, it was found that hydrogen and hydrogen-donor atmospheres promote olefin saturation, enhance the paraffin yield, and improve distillable hydrocarbon fractions (343 °C–). The spent catalyst regenerated ex situ by oxidising the deposited asphaltenes and coke lost 52.5% of the surface area compared with the fresh catalyst. However its upgrading performance in terms of change in API gravity, viscosity reduction and the yield of distillable was similar to that of the fresh catalyst.

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#### References

- [1] International Energy Agency IEA, World energy outlook, ISBN: 978 9264 12413 4, November, 2011.
- [2] Das KS, Butler MR. Mechanism of the vapour extraction process for heavy oil and bitumen. *J Pet Sci Eng* 1998;21:43–59.
- [3] Sorrel S, Speirs J, Bentley R, Brandt A, Miller R. Global oil depletion: a review of the evidence. *Energy Policy* 2010;38:5290–5.
- [4] Sena MFMd, Rosa LP, Szklo A. Will Venezuelan extra-heavy oil be a significant source of petroleum in the next decades? *Energy Policy* 2013;61:51–9.
- [5] Carrillo AJ, Corredor ML. Upgrading of heavy crude oils: Castilla. *Fuel Process Technol* 2013;109:156–62.
- [6] Hedrick BW, Seibert KD, Crewe CA. New approach to heavy oil and bitumen upgrading, Report No. AM-06-29, UOP LLC, Illinois: Des Plaines; 2006.
- [7] Shen Z, Cao Z, Zhu X, Li X. Visbreaking of Chinese oil sands bitumen. *Pet Sci Technol* 2008;26:1676–83.
- [8] Hsu C, Robinson P. Practical advances in petroleum processing, 1. Springer Science+Business Media, Inc.; 2006. p. 22.
- [9] Leyva C, Mohan SR, Fernando T, Ancheyta J. On the use of acid-base-supported catalysts for hydroprocessing of heavy petroleum. *Ind Eng Chem Res* 2007;46:7448–66.
- [10] Longstaff DC, Deo MD, Hanson FV. Hydrotreatment of bitumen from the Whitefrocks oil sands deposit. *Fuel* 1994;73(9):1523–30.
- [11] Liu K, Fung CS, Ho CT, Rumschitzki SD. Hydrogasification of coke in heptane reforming over Pt–Re/Al<sub>2</sub>O<sub>3</sub>. *Ind Eng Chem Res* 2003;42:1543–50.
- [12] Xia TX, Greaves M, Werfilli WS, Rathbone RR. Downhole conversion of Lloydminster heavy oil using THAI–CAPRI process, SPE/Petroleum Society of CIM/CHOA 78998, Presented at International Horizontal Well Technology Conference 2002, Calgary, Canada, November 4–7, 2002.
- [13] Xia TX, Greaves M. 3-D physical model studies of downhole catalytic upgrading of Wolf Lake heavy oil using THAI. CIPC paper 2001-017 Presented at the Petroleum Society's Canadian Internal Petroleum Conference 2001, Calgary, Canada, June 12–14, 2001.
- [14] Greaves M, Dong LL, Rigby SP. Simulation study of the Toe-to-Heel air injection three-dimensional combustion cell experiment and effect in the mobile oil zone. *Energy Fuels* 2012;26:1656–69.
- [15] Hart A, Shah A, Leeke G, Greaves M, Wood J. Optimization of the CAPRI process for heavy oil upgrading: effect of hydrogen and guard bed. *Ind Eng Chem Res* 2013;52:15394–406.
- [16] Wenlong G, Xi C, Chen Y, Zhang X, Muhetar LJ, Huang J, et al. Fire-flooding technologies in post-steam-injected heavy oil reservoirs. *Petrol Explor Dev* 2011;38(4):452–62.

- [17] Shah A, Fishwick RP, Leeke GA, Wood J, Rigby SP, Greaves M. Experimental optimisation of catalytic process in situ for heavy-oil and bitumen upgrading. *J Can Petrol Technol* 2011;50(11–12):33–47.
- [18] Ancheyta J, Rana SM, Furimsky E. Hydroprocessing of heavy petroleum feeds: tutorial. *Catal Today* 2005;109:3–15.
- [19] Aleman-vazquez LO, Cano-Dominguez JL, Garcia-Gutierrez JL. Effect of tetralin, decalin and naphthalene as hydrogen donors in the upgrading of heavy oils. *Procedia Eng* 2012;42:532–9.
- [20] Ovalles C, Filgueiras E, Morales A, Rojas I, Jesus de JC, Berrios I. Use of a dispersed molybdenum catalyst and mechanistic studies for upgrading extra-heavy crude oil using methane as source of hydrogen. *Energy Fuels* 1998;12:379–85.
- [21] Ovalles C, Filgueiras E, Morales A, Scott EC, Gonzalez GF, Pierre EB. Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen. *Fuel* 2003;82:887–92.
- [22] Liu D, Li Z, Fu Y, Zhang Y, Gao P, Dai C, et al. Investigation on asphaltene structures during Venezuela heavy oil hydrocracking under various hydrogen pressures. *Energy Fuels* 2013;27:3692–8.
- [23] Ancheyta J, Betancourt G, Marroquin G, Centeno G, Castaneda LC, Alonso F, et al. Hydroprocessing of Maya heavy crude oil in two reaction stages. *Appl Catal, A* 2002;233:159–70.
- [24] Maity SK, Blanco E, Ancheyta J, Alonso F, Fukuyama H. Early stage deactivation of heavy crude oil hydroprocessing catalysts. *Fuel* 2012;100:17–23.
- [25] Hollander dMA, Makkee M, Moulijn JA. Coke formation in fluid catalytic cracking studies with the microriser. *Catal Today* 1998;46:27–35.
- [26] Qi W, Lei G, Zong-xian W, Bao-quan M, Ai-jun G, He L. Hydrogen donor visbreaking of Venezuela vacuum residue. *J Fuel Chem Technol* 2012;40(11):1317–22.
- [27] Zhao S, Kotlyar SL, Woods RJ, Sparks DB, Chung HK. Effect of thermal and hydro-catalytic treatment on the molecular chemistry of narrow fractions of Athabasca bitumen pitch. *Energy Fuels* 2001;15:113–9.
- [28] Gray RM, Zhao Y, McKnight MC, Komar AD, Carruthers DJ. Coking of hydroprocessing catalyst by residue fractions of bitumen. *Energy Fuels* 1999;13:1037–45.
- [29] Puron H, Pinilla LJ, Berruero C, Fuente de la Montoya JA, Millan M. Hydrocracking of Maya vacuum residue with NiMo catalysts supported on mesoporous alumina and silica–alumina. *Energy Fuel* 2013;27:3952–60.
- [30] Hart A, Leeke G, Greaves M, Wood J. Down-hole catalytic upgrading of heavy oil and bitumen to meet tomorrow's energy needs: the THAI–CAPRI process. In: *Proceeding of the third North Am Symp Chem React Eng* March 17–20, 2013, Houston, Texas; 2013.